

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-193054

(43)Date of publication of application : 30.07.1996

(51)Int.Cl.

C07C 69/712

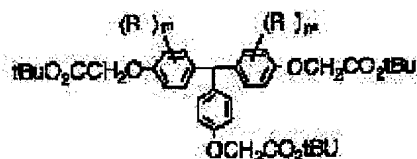
G03F 7/004

H01L 21/027

(21)Application number : 07-020955

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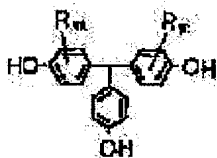
(22)Date of filing : 13.01.1995

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YAGIHASHI FUJIO(54) BIS(4-T-BUTOXYCARBONYLMETHYLOXY-2,5-DIMETHYLPHENYL)
METHYL-4-T-BUTOXYCARBONYLMETHYLOXYBENZENE AND ITS DERIVATIVE

(57)Abstract:

PURPOSE: To obtain the subject compound having a specific mother nucleus structure and t-butoxycarbonylmethyl ether side chains, having high compatibility with polymeric compounds, and useful as a dissolution inhibitor for positive resists.

CONSTITUTION: The compound of formula I (R is alkyl; m is 0-4). The compound of formula I is preferably obtained e.g. by dissolving a bis(4-hydroxyphenylmethyl)methyl-4-hydroxybenzene of formula II, e.g. bis(4-hydroxy-2,5-dimethylphenyl)methyl-4-hydroxybenzene, in DMF and subsequently reacting the compound of formula II with t-butyl chloroacetate in the presence of potassium carbonate at 60-100° C for 4-8hr, etc.



II.

LEGAL STATUS

[Date of request for examination]

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[Kind of final disposal of application other than the
examiner's decision of rejection or application]

converted registration]

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[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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[Date of extinction of right]

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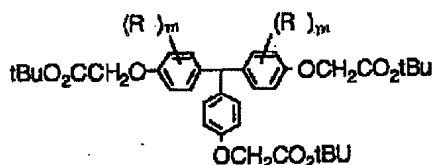
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The bis(4-t-butoxy cull BONIRUMECHIROKISHI -2, 5-dimethylphenyl) methyl-4-t-butoxy cull BONIRUMECHIROKISHI benzene expressed with the following-ization 1, and its derivative;

[Formula 1]



[Industrial Application] This invention relates to the effective new molecular entity as a lysis inhibition agent especially used for positives resist about a new compound.

[0002]

[Description of the Prior Art] Generally performing micro processing, such as a semi-conductor, conventionally using a resist is performed. In this case, in order that resolution may go up so that the radiation of short wavelength, such as high energy ultraviolet rays, an electron ray, and an X-ray, is used and wavelength becomes short, in order to acquire the process tolerance of 0.3 micrometers or less, developing a suitable resist to the radiation of short wavelength more is called for.

[0003] these radiations are used and the so-called chemistry magnification mold resist proposes as one approach for obtaining the resist of high sensitivity and high resolution -- having -- [H.Ito et al., Polym.Eng.Sci., 23 volumes, and 1023 pages (1983)] -- it has been observed. Especially this chemistry magnification mold resist in a positive type ** The two-component system resist which makes an indispensable constituent the high molecular compound which decomposes with an acid and becomes alkali fusibility although it does not dissolve in the compound which absorbs a radiation and generates an acid, and an alkali water solution (JP,2-209977,A etc.), ** The high molecular compound which decomposes with the compound, alkali fusibility high molecular compound, or acid which generates an acid with a radiation, and serves as alkali fusibility, And it is divided roughly into 3 component system resists (JP,2-245756,A etc.) which make an indispensable constituent the lysis inhibition agent which prevents the alkali dissolution of this high molecular compound, and decomposes with an acid, and loses this dissolution stopping power.

[0004] The imaging mechanism of 3 component system resist forms a positive image, when the very small acid which absorbs the irradiated radiation and is generated is made into a catalyst, a chemical reaction occurs in the both sides of a lysis inhibition agent or a lysis inhibition agent, and a high molecular compound and the solubility over the alkali developer of a high molecular compound increases only about the part where the radiation was irradiated by that cause.

[0005] Although very high practical sensibility was realized by the mechanism of such a chemistry magnification mold resist as compared with the conventional resist Since it is spread from [after an alkaline impurity advances from a resist front face and a substrate and irradiates a radiation] before development, an acid deactivates. The part which deactivated had the fault of producing the case where it becomes impossible to dissolve in an alkaline developer, and an exact image cannot be formed even if a radiation is irradiated.

[0006] It originates in this fault and the phenomenon in which a canopy top, such as T top, is formed in a pattern, or Susono called skirt length is made to a pattern near a substrate side is observed near the surface of a resist. For this reason, a chemical reaction occurs with the acid for which the radiation was irradiated and which was generated as engine performance required of a lysis inhibition agent, and not only the engine performance that enlarges the dissolution rate ratio of the part by which the radiation was irradiated, and the part which is not irradiated but when membranes are formed as a resist, the engine performance which makes late threshold speed to the inside of the film of an alkaline impurity is also required.

[0007] In order to fill the above-mentioned demand, it is desirable for a lysis inhibition agent to have high compatibility to a high molecular compound, and to have comparatively higher lipophilicity. However, many of lysis inhibition agents [no] announced until now were what can fill these demands completely.

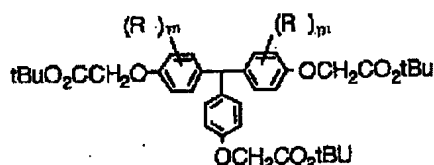
[0008]

[Problem(s) to be Solved by the Invention] Then, when this invention etc. compounds various compounds, a resist is prepared and the engine performance is examined, while finding out a series of mother-nucleus structures excellent in compatibility with a high molecular compound By using the t-butoxy carbonylmethyl ether as a side chain, it found out that contrast with high exposure part and non-irradiating part can be acquired, and that the resistance over penetration of an alkaline impurity could be given, and this invention was reached. Therefore, the purpose of this invention is to offer the effective new compound as a lysis inhibition agent for a positive resist especially.

[0009]

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the bis(4-t-butoxy cull BONIRUMECHIROKISHI -2, 5-dimethylphenyl) methyl-4-t-butoxy cull BONIRUMECHIROKISHI benzene expressed with the following-ization 2, and its derivative.

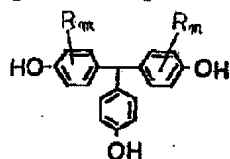
[Formula 2]



However, R in ** 2 expresses an alkyl group, and m expresses the integer of 0-4.

[0010] The compound of this invention is a screw (after dissolving 4-hydroxy phenylmethyl-4-hydroxybenzene or its derivative in a suitable solvent, it is easily compoundable by heating and stirring tert butyl chloroacetate and potassium carbonate moreover.) expressed with the following-ization 3.

[Formula 3]



[0011] R3 As an example, although a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, t-butyl, a pentyl radical, a neopentyl radical, a hexyl group, etc. can be mentioned, for example, a methyl group and an ethyl group are desirable also especially in these. Moreover, as for m, it is desirable that it is 0, 1, or 2. As a solvent used at the time of composition, although DMF, DMSO, an acetone, etc. can be mentioned, it is desirable to use DMF also especially in these.

[0012] moreover, tert butyl chloroacetate -- or although it can change to it and bromoacetic acid-t-butyl, iodoacetic acid-t-butyl, etc. can also be used, it is desirable to use tert butyl chloroacetate from viewpoints, such as acquisition ease, handling nature, and reactivity. the same -- potassium carbonate -- or although it can change to potassium carbonate and a sodium carbonate, a lithium carbonate, etc. can also be used, it is desirable to use potassium carbonate or a sodium carbonate especially from viewpoints, such as reactivity.

[0013] Especially as long as the amount of these reactants used is more than the amount of theory that

needs tert butyl chloroacetate, potassium carbonate, etc. to obtain the specified substance, it is not restricted, but since the above-mentioned reaction advances quantitatively, use of the amount of theory is sufficient. Although a reaction is performed stirring among 40 degrees C – 120 degrees C, it is desirable from compaction of reaction time, and a viewpoint of yield to make it react at 60 degrees C – 100 degrees C especially, and, as for the concentration of reaction mixture, it is desirable that it is 10 % of the weight – 50 % of the weight. If it is these reaction conditions, a reaction will be ended in 4 hours – 8 hours. It can perform easily carrying out separation purification of the specified substance from the reaction mixture after reaction termination by combining a well-known approach suitably.

[0014] Since the compound of this invention is easily desorbed from a t-butoxy carbonylmethyl ether group and becomes alkali fusibility under existence of an acid while it has the mother-nucleus structure excellent in compatibility with a high molecular compound, it is especially effective as a lysis inhibition agent of the positive-resist ingredient of 3 component system.

[0015] The positive-resist ingredient of 3 component system is constituted by (A) lysis inhibition agent, the (B) acid generator, the (C) high molecular compound, and the (D) solvent like common knowledge. In this case, the weight ratio of A:B:C:D is 5-50:0.5-30:70-90:150-700, and is 10-25:2-8:75-85:250-500 preferably.

[0016]

[Effect of the Invention] Since the compound of this invention has high compatibility to a high molecular compound, it can be used in large quantities as a dissolution inhibitor into 3 component positive resist. Moreover, since lipophilicity is high, it has the effectiveness which an alkali impurity makes it hard to advance into the resist film from a resist front-face and substrate side.

[0017]

[Example] Hereafter, this invention is not limited by this although an example explains this invention to a detail further.

example 1. bis(4-hydroxy - 2, 5-dimethylphenyl) methyl-4-hydroxybenzene 3.5g (0.01 mols) — DMF50g — dissolving — 4.5g (0.03 mols) of tert butyls chloroacetate, and 4.1g (0.03 mols) of potassium carbonate — in addition, 6-hour heating and stirring of were done at 80 degrees C.

[0018] After adding and washing 100g of water further to the toluene phase which added toluene 50g and 100g of water, and was separated after cooling reaction mixture radiationally and drying with magnesium sulfate, when reduced pressure distilling off of the solvent was carried out, the oil-like reaction mixture was obtained. When the silica gel column chromatography (elution solvent: chloroform) refined this, bis(4-t-butoxy cull BONIRUMECHIROKISHI -2, 5-dimethylphenyl) methyl-4-t-butoxy cull BONIRUMECHIROKISHI benzene 5.2g (76% of yield) was obtained as a colorless crystal.

[0019] The melting point is 106-108 degrees C, and is the following. It was checked from delta value of ¹H-NMR, and the result of elemental analysis that it is the above-mentioned compound.

¹H-NMR delta1.48 (s27H and t-bu-CH₃) and delta2.05 (s6H —) - Ph -CH₃, delta 2.12 (s6H and -Ph-CH₃), delta4.49 (s2H and -OCH₂ CO), delta4.50 (s4H and -OCH₂ CO), delta5.42 (s1H, Ph₃-CH), delta6.45 (s2H, Ph-H), delta6.48 (s2H, Ph-H), delta6.79 (d2H, Ph-H), delta6.87 (d2H, ph-H)

Elemental analysis (%)

Analysis value C:71.50, H:7.98 theoretical value C:71.28, H:7.88

[Translation done.]